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## (54) CEMENT ADMIXTURE

## (57)Abstract:

PURPOSE: To obtain a cement mixture excellent in slumploss preventing effect and high in water reducing property and excellent in operability by incorporating the specified esterification reaction product containing a polyoxyalkylene deriv. as an active principle.

CONSTITUTION: The cement admixture is composed as an active principle of the esterification reaction product of (A) the copolymer consisting of (a) the polyoxyalkylene deriv. expressed by formula I (A1O is (2-4)C oxyalkylene containing 50-100mol.% oxyethylene, R1 is (1-4)C alkyl, n is 4-150) and (b) maleic anhydride as indispensable constituents and (B) the polyoxyalkylene deriv. expressed by formula II (R2 is (2-5)C alkenyl, A2O is (2-4)C oxyalkylene, m is 1-300). The admixture is excellent in slumploss preventing effect and high in water reducing property and excellent in operability.



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CLAIMS

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[Claim(s)]

[Claim 1] (A) -- (\*\*) -- general formula CH<sub>2</sub>=CHCH<sub>2</sub>O(A<sub>1</sub>O) nR<sub>1</sub> (the oxy-alkylene group of the carbon numbers 2-4 the 50-100-mol% of whose of A<sub>1</sub>O in a formula is an oxyethylene radical --) R<sub>1</sub> -- the alkyl group of carbon numbers 1-4, and n -- the integer of 4-150 -- it is -- with the copolymer which makes an indispensable monomer the polyoxyalkylene derivative expressed and a (b) maleic anhydride (B) Additive for cement which makes an active principle an esterification reactant with the polyoxyalkylene derivative expressed with general formula R<sub>2</sub>O(A<sub>2</sub>O) mH (R<sub>2</sub> in a formula is [ the oxy-alkylene group of carbon numbers 2-4 and m of the alkenyl radical of carbon numbers 2-5 and A<sub>2</sub>O ] the integers of 1-300).

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

## [0001]

[Industrial Application] This invention relates to the new additive for cement, and the additive for the cement which it excels in the slump loss prevention effectiveness in more detail, and whose water reducing nature is large, and is satisfactory on the occasion of use.

## [0002]

[Description of the Prior Art] Conventionally, the naphthalene sulfonic-acid formaldehyde condensate salt, the melamine sulfonic-acid formaldehyde condensate salt, the ligninsulfonic acid salt, etc. are used as the additive of cement compounds, such as concrete, for example, a water reducing agent. The demand of high intensity increases to concrete in recent years, and the need of lessening the amount of the water in a concrete constituent came out. Although it had the effectiveness that the above-mentioned additive lessened the amount of the water of a concrete constituent, there was a problem that the fluid fall of the concrete constituent which happens with time, and the so-called slump loss were unavoidable. In order to prevent this slump loss, the proposal of former versatility is made. For example, the compound of fine-particles-like an olefin / maleic-anhydride copolymer, and water reducing agents, such as a naphthalene sulfonic-acid formalin condensate salt, is indicated (JP,60-16851,A). However, separation tends to produce this compound and it has the fault of becoming an ununiformity. Moreover, although it is indicated that concomitant use with a naphthalene sulfonic-acid formalin condensate salt or a melamine sulfonic-acid formalin condensate salt, and an allyl alcohol alkylene oxide addition product / partial saturation dicarboxylic acid copolymer is effective in prevention of slump loss (JP,59-162162,A), about the effectiveness, it cannot necessarily be said that it is enough. Furthermore, although the copolymer of the polyoxyalkylene partial saturation ether and a maleic anhydride, its hydrolyzate, or the salt of that hydrolyzate is proposed (JP,63-285140,A), the field of prevention of slump loss in this case is not necessarily enough. On the other hand, the copolymer of the polyoxyalkylene partial saturation ether and a maleate is proposed (JP,2-163108,A). However, in this copolymer, when the alcohol which forms ester is two or more organic functions, it is hard to use it for water, being insoluble or refractory in it, and in the case of one organic functions, there is a fault that the setting time becomes long. Such slump loss is a big problem in the concrete industry, and quick solution was desired.

## [0003]

[Problem(s) to be Solved by the Invention] This invention is the basis of such a situation and it excels in the prevention effectiveness of slump loss, and water reducing nature is large and it is made for the purpose of offering the additive for cement which is satisfactory on the occasion of use.

## [0004]

[Means for Solving the Problem] As a result of repeating research wholeheartedly that the additive for cement which has the aforementioned desirable property should be developed, this invention persons find out that what makes a specific esterification reactant an active principle may suit that purpose, and came to complete this invention based on this knowledge. namely, this invention -- (A) (\*\*) -- general formula  $\text{CH}_2=\text{CHCH}_2\text{O}(\text{A}_1\text{O})_n\text{R}_1$  [-- 1]

the polyoxyalkylene derivative and (\*\*) which are expressed with (the alkyl group of carbon numbers 1-4 and n of the oxy-alkylene group of the carbon numbers 2-4 the 50 - 100-mol% of whose of A1O in a formula is an oxyethylene radical, and R1 are the integers of 4-150) -- copolymer which makes a maleic anhydride an indispensable monomer, and (B) general formula R2O(A2O) mH [-- 2]

The additive for cement which makes an active principle an esterification reactant with the polyoxyalkylene derivative expressed with (R2 in a formula is [ the oxy-alkylene group of carbon numbers 2-4 and m of the alkenyl radical of carbon numbers 2-5 and A2O ] the integers of 1-300) is offered. Hereafter, this invention is explained to a detail. It sets to the copolymer of a \*\* (A) component by making the esterification reactant of the copolymer of the (A) component, and the polyoxyalkylene derivative of the (B) component into an active principle, and the additive for cement of this invention is general formula CH<sub>2</sub>=CHCH<sub>2</sub>O(A1O) nR1 as an indispensable monomer. -- [1]

The polyoxyalkylene derivative and maleic anhydride as which A1O in a formula, and R1 and n are expressed (with the same semantics as the above) are used. In said general formula [1], as an oxy-alkylene group of the carbon numbers 2-4 shown by A1O, an oxyethylene radical, an oxypropylene radical, an oxy-butylene radical, and an oxy-tetramethylen radical are mentioned, and the 50 - 100-mol % is an oxyethylene radical. Since water solubility becomes inadequate when this oxyethylene radical is less than [ 50 mol % ], high water reducing nature cannot be obtained. Moreover, as an alkyl group of the carbon numbers 1-4 shown by R1, a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, an isobutyl radical, sec-butyl, and t-butyl are mentioned. Furthermore, n is the integer of 4-150, if the setting time becomes late less than by four and this n exceeds 150, viscosity will become high and it will become difficult to manufacture it. On the other hand, as a polyoxyalkylene derivative of the (B) component, it is general formula R2O(A2O) mH. -- [2]

The compound by which R2, A2O, and m in a formula are expressed (with the same semantics as the above) is used.

[0005] In said general formula [2], a vinyl group, an allyl group, an isopropenyl radical, a butenyl group, a pentenyl radical, etc. are mentioned as an alkenyl radical of the carbon numbers 2-5 shown by R2. Moreover, as an oxy-alkylene group of the carbon numbers 2-4 shown by A2O, an oxyethylene radical, an oxypropylene radical, an oxy-butylene radical, and an oxy-tetramethylen radical are mentioned. The copolymer of the compound and maleic anhydride which are expressed with said general formula [1] can be easily manufactured by carrying out copolymerization of the compound and maleic anhydride which are expressed with this general formula [1] using a peroxide system initiator or an azo system initiator. Copolymerization of the monomer of the alpha olefin in that case, for example, styrene, an acrylic acid, a methacrylic acid, acrylic ester, methacrylic ester, vinyl acetate, etc. which can be copolymerized may be mixed and carried out. the operating rate of the compound and maleic anhydride which are expressed with this general formula [1] -- a mole ratio -- usually -- 1:0.5 thru/or 1:2 -- it is preferably chosen in 1:0.9 thru/or 1:2. Thus, although the esterification reaction of the compound expressed with the copolymer of the (A) component and the general formula [2] of the (B) component which were obtained is carried out, as a ratio with the hydroxyl equivalent of the compound expressed with the maleic-anhydride residue equivalent and the general formula [2] of this copolymer in this case is in the range of 1:2 thru/or 10:1, it is good to use both components. The reactant with the compound expressed with the copolymer of the aforementioned (A) component and the general formula [2] of the (B) component is completeness or a partial esterification object, for example, can be easily obtained by making it react to the bottom of existence of acid catalysts, such as basic catalysts, such as a sodium hydroxide, a potassium hydroxide, and sodium methylate, or a phosphoric acid, phosphorous acid, a sulfuric acid, p-toluenesulfonic acid, and methansulfonic acid. Moreover, it can obtain also by heating with a non-catalyst. The additive for cement of this invention is usually preferably used at 0.04 - 1% of the weight of a rate 0.01 to 3% of the weight to cement by making into an active principle the esterification reactant which is the above, and was made and obtained. Moreover, this invention additive may be used together with other additives, such as for example, a naphthalene sulfonic-acid formaldehyde condensate salt, a melamine sulfonic-acid formaldehyde condensate salt, and a polycarboxylic acid system compound, or a defoaming agent, an air entraining agent, a rusr-proofer, a

setting accelerator, retarding admixture, etc. Furthermore, on this invention additive, alkali, such as a potassium hydroxide, a sodium hydroxide, and a calcium hydroxide, amines, etc. may be added according to a request for pH adjustment.

[0006]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples.

The copolymer of the compound of a general formula [1] and a maleic anhydride is shown in the example 1 of manufacture - the 11 1st table. It taught the 4 opening flask to which an agitator, nitrogen entrainment tubing, a thermometer, and reflux tubing were attached by the ratio which shows the copolymer and the compound of a general formula [2] shown in the 2nd table in the 2nd table.

Furthermore, added 0.1 % of the weight of sodium methylates to this copolymer, it was made to react at 100 degrees C for 3 hours, and the esterification object was obtained. The weight average molecular weight of the esterification object is shown in the 2nd table.

[0007]

[Table 1]

第1表

共重合 体名	一般式 [1] の化合物	(モル)	無水マレイン酸 (モル)	他の单量体 (モル)	重畳平均 分子量 <sup>g)</sup>
A	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> CH <sub>3</sub>	(1.0)	1.0	-	18.000
B	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>33</sub> CH <sub>3</sub>	(1.0)	1.0	-	20.000
C	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>110</sub> CH <sub>3</sub>	(1.0)	1.0	-	30.000
D	CH <sub>2</sub> =CHCH <sub>2</sub> O[(C <sub>3</sub> H <sub>6</sub> O) <sub>13</sub> (C <sub>2</sub> H <sub>4</sub> O) <sub>15</sub> ]C <sub>4</sub> H <sub>9</sub> <sup>11</sup>	(1.0)	1.0	-	24.000
E	CH <sub>2</sub> =CHCH <sub>2</sub> O[(C <sub>2</sub> H <sub>4</sub> O) <sub>46</sub> (C <sub>4</sub> H <sub>6</sub> O) <sub>16</sub> ]C <sub>4</sub> H <sub>9</sub> <sup>112</sup>	(1.0)	1.0	-	22.000
F	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>3</sub> H <sub>6</sub> O) <sub>5</sub> (C <sub>2</sub> H <sub>4</sub> O) <sub>30</sub> CH <sub>3</sub>	(1.0)	1.0	-	23.000
G	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> CH <sub>3</sub>	(0.9)	1.0	スチレン(0.1)	18.000

- [0008] Notes 1[ ] It is shown that inside is a random-like adduct.  
 2) C<sub>4</sub>H<sub>8</sub>O shows an oxy-tetramethylen radical.  
 3) It asked from gel permeation chromatography.

[0009]

[Table 2]

第2表

製造例	共重合体名(重量%)	一般式 [2] の化合物	(重量%)	重量平均 分子量 <sup>a)</sup>
1 A	(54.0)	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(47.0)	27.000
2 B	(74.5)	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(25.5)	29.000
3 B	(82.9)	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(17.1)	25.000
4 B	(51.8)	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>33</sub> H	(48.2)	28.000
5 B	(39.8)	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>110</sub> H	(60.2)	31.000
6 C	(90.0)	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(10.0)	33.000
7 D	(52.3)	CH <sub>2</sub> =CHCH <sub>2</sub> O[(C <sub>2</sub> H <sub>4</sub> O) <sub>15</sub> (C <sub>3</sub> H <sub>6</sub> O) <sub>16</sub> ]H <sup>b)</sup>	(47.7)	28.000
8 E	(50.1)	CH <sub>2</sub> =CHCH <sub>2</sub> O[(C <sub>2</sub> H <sub>4</sub> O) <sub>40</sub> (C <sub>4</sub> H <sub>8</sub> O) <sub>10</sub> ]H <sup>b)</sup>	(49.9)	29.000
9 F	(53.9)	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>33</sub> H	(46.1)	28.000
10 G	(51.7)	CH <sub>2</sub> =C(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(48.3)	26.000
11 G	(35.4)	CH <sub>2</sub> =CHCH <sub>2</sub> O(C <sub>2</sub> H <sub>4</sub> O) <sub>11</sub> H	(64.6)	29.000

[0010] Notes 1, 2, and 3 are the same as the footnote of the 1st table.

Other additives shown with the esterification object shown in the example 12 of manufacture - the 15 2nd table in the 3rd table were mixed by the ratio shown in the 3rd table.

[0011]

[Table 3]

第3表

製造例	第2表で示した反応物（重量%）	他の添加物 (重量%)
12	製造例3 (30.0)	ナフタレンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
13	製造例3 (30.0)	メラミンスルホン酸ホルマリン 縮合物ナトリウム塩 (70.0)
14	製造例4 (50.0)	第1表に示す共重合体A (50.0)
15	製造例3 (50.0)	第1表に示す共重合体B (50.0)

[0012] The trial by concrete was carried out using the reactant and mixture which were shown in an example 1 - the examples 1-15 of 15 manufactures. A combination presentation and a test condition are shown below.

Combination presentation (kg/m<sup>3</sup>)

Water 166 cement 450 sand 681 crushed stones 1032 additives It is shown in the 4th table.

Water / cement ratio 36.9wt% fine total aggregate ratio It took out, after kneading each component of the 39.9wt% above for 2 minutes for a pan mixer, and the slump and the air content were measured. Furthermore, it moved to the collapse type mixer, and mixed by per minute 2 rotation, and the slump and air content of 30 minutes, 60 minutes, and 90 minutes after were measured. Moreover, it measured also about the setting time and compressive strength, and these results were shown in the 4th table.

The same trial as examples 1-15 was performed by making into the example of a comparison the compound shown in the 1-6th examples of a comparison. The result is shown in the 4th table.

Example 1 of a comparison Example 2 of a naphthalene sulfonic-acid formalin condensate sodium salt comparison Example 3 of a polyethylene-glycol monoallyl ether maleic-acid copolymer sodium salt comparison Compound 75wt% of the example 1 of a comparison The example [ of a comparison / 2 / compound 25wt% of ] example 4 of a mixture comparison The compound of the general formula [1] used by the copolymer name A of the 1st table The polyoxyethylene monomethyl ether of a maleic acid Example 5 of a copolymer comparison with the esterification object by (average molecular weight 550)

Example 6 of a copolymer comparison of the compound of the general formula [1] used by the copolymer name A of the 1st table, and the esterification object by the polyethylene glycol (average molecular weight 1030) of a maleic acid With no additive. However, only the example 6 of a

comparison carries out a combination presentation as follows. Combination presentation (kg/m<sup>3</sup>)

Water 195 cement 450 sand 652 crushed stones 985 water / cement ratio 43.3wt% fine total aggregate ratio 40.0wt% [0013]

[Table 4]

第4表-1

	添加量 (対セメントwt%)	スランプ(cm)				空気量(%)				
		混練直後	30分後	60分後	90分後	混練直後	30分後	60分後	90分後	
実施例	1	0.28	18.0	19.0	19.5	18.5	4.0	4.2	4.1	4.2
	2	0.26	18.5	19.0	19.0	18.0	3.9	4.0	4.0	4.1
	3	0.25	18.0	19.5	19.5	19.0	4.0	4.2	4.2	4.2
	4	0.32	17.5	19.0	20.0	19.5	3.9	4.1	4.3	4.2
	5	0.36	18.0	18.5	19.0	18.0	4.0	4.1	4.2	4.2
	6	0.31	18.5	19.5	20.5	20.0	4.0	3.9	4.0	4.0
	7	0.34	18.5	18.5	18.5	18.0	4.1	4.1	4.2	4.3
	8	0.38	17.5	18.5	17.5	17.0	4.1	4.0	3.9	4.0
	9	0.36	18.0	19.0	19.0	18.5	3.9	4.0	4.2	4.1
	10	0.29	17.5	19.0	20.0	19.0	4.0	4.2	4.1	4.0
	11	0.48	18.0	18.0	17.5	17.0	4.0	4.0	3.8	3.8
	12	0.56	18.5	17.5	17.0	16.5	4.1	4.0	4.0	3.8
	13	0.23	18.0	19.0	18.5	17.5	4.0	3.9	3.9	3.9
	14	0.25	18.0	18.5	18.5	17.5	3.9	4.1	4.0	3.9
	15	0.28	18.5	19.0	19.0	18.5	4.0	4.0	3.9	3.8
比較例	1	0.75	18.0	15.5	12.5	11.5	4.0	3.8	3.7	3.6
	2	0.60	17.5	16.5	14.5	12.5	4.0	4.1	3.9	4.0
	3	0.70	18.0	16.0	13.5	12.0	3.9	4.0	3.9	3.9
	4	0.50	18.0	18.5	18.0	17.5	4.0	4.2	4.1	4.0
	5	0.65	16.0	16.5	15.0	14.5	4.2	4.2	3.9	4.1
	6	-	17.5	16.5	15.5	14.0	4.1	3.9	3.9	3.8

[0014]  
[Table 5]

第4表-2

		凝結時間(時間一分)		圧縮強度(kgf/cm <sup>2</sup> )		
		始発	終結	3日	7日	28日
実 施 例	1	6-20	8-10	458	630	780
	2	5-45	7-40	465	639	800
	3	6-00	7-50	467	637	796
	4	6-05	8-05	463	632	805
	5	5-55	7-55	462	635	786
	6	5-30	7-20	480	645	788
	7	7-15	8-45	455	618	768
	8	6-55	8-45	461	630	764
	9	7-25	9-20	452	619	766
	10	6-20	8-00	476	633	791
	11	6-05	8-20	468	622	779
	12	6-10	8-20	445	634	775
	13	5-30	7-10	460	635	801
	14	5-20	7-20	468	648	799
	15	5-45	7-40	455	618	780
比較 例	1	5-50	7-30	437	614	751
	2	9-05	10-55	419	613	755
	3	7-50	9-35	433	625	757
	4	9-50	11-55	446	637	787
	5	12-10	14-00	365	418	556
	6	5-15	7-00	312	467	605

[0015] To a slump index becoming small with time and the fluidity of the examples 1, 2, 3, and 5 of a comparison being lost, a slump index does not become small with time, but, as for examples 1-15, the fluidity is held. Coagulation start time becomes late and, as for the examples 2, 4, and 5 of a comparison, the setting time is late. Moreover, when you have no additive of the example 6 of a comparison, unless it makes [ many ] moisture, it cannot knead, but if the additive of this invention is used to the compressive strength of molding becoming small, there are few moisture contents, and it can knead, and compressive strength becomes large.

[0016]

[Effect of the Invention] While the additive for cement of this invention makes an active principle the completeness or the partial esterification object of the copolymer of the polyoxyalkylene derivative of copolymerization nature, and a maleic anhydride, and the specific polyoxyalkylene derivative which has an alkenyl radical and excelling in the slump loss prevention effectiveness, water reducing nature is large and has the descriptions, such as excelling also in workability.

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